Electronic Supplementary Material (ESI) for Molecular Systems Design & Engineering.


# Supporting Information

# Descriptors of Transition Metal Promoters on $MoS_2$ Nanocatalysts for Hydrodesulfurization: Binding Energy of Metal Sulfides from First Principles

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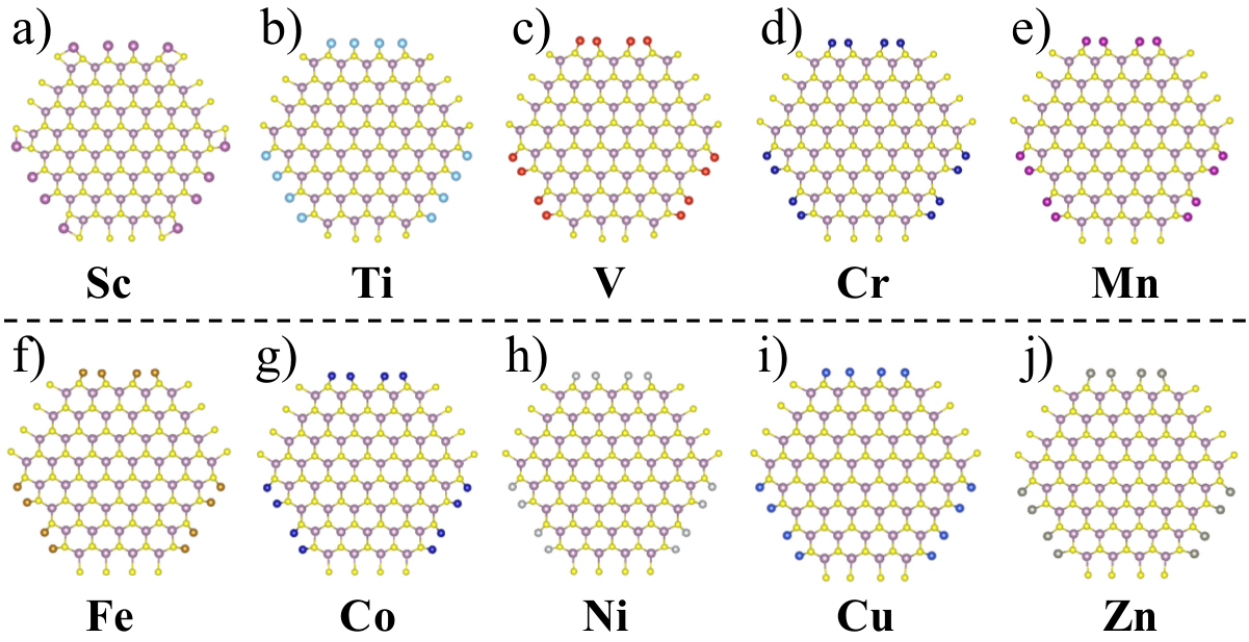


**Fig. S1** Geometrical structures of the relaxed TM-promoted MoS2 nanosheets without sulfur saturation, with the 3d TM promoters; a) Sc, b) Ti, c) V, d) Cr, e) Mn, f) Fe, g) Co, h) Ni, i) Cu, and j) Zn.

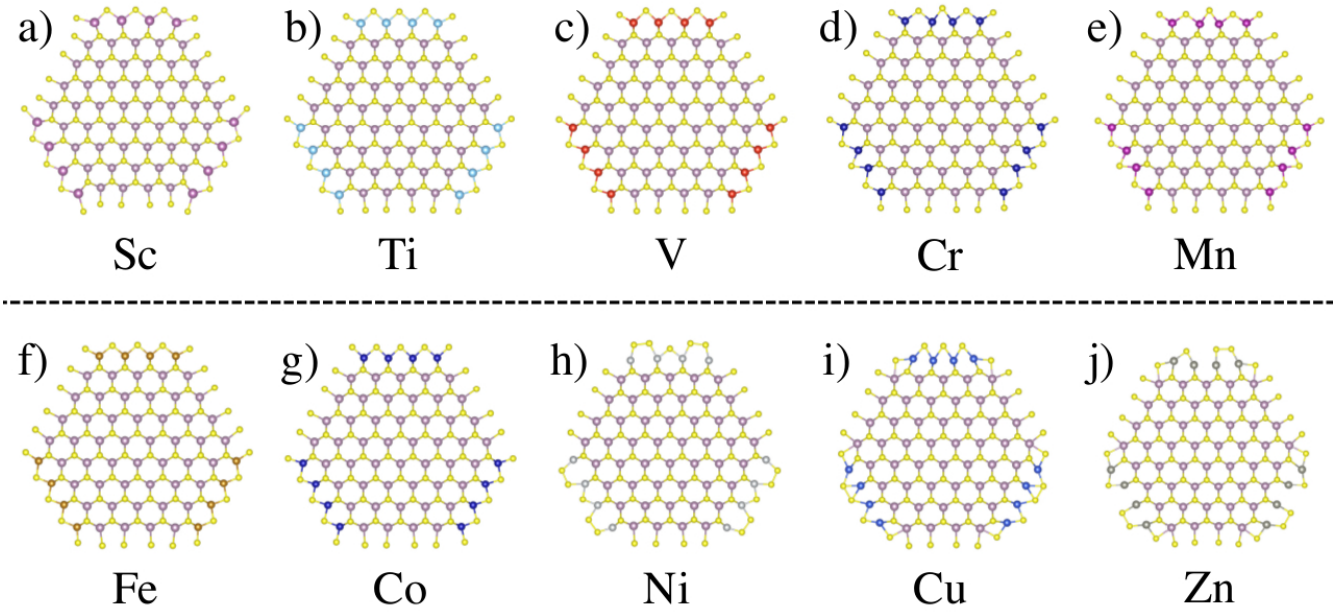


**Fig. S2** Geometrical structures of the relaxed TM-promoted $MoS_2$ nanosheets with sulfur saturation, with the 3*d* TM promoters; a) Sc, b) Ti, c) V, d) Cr, e) Mn, f) Fe, g) Co, h) Ni, i) Cu, and j) Zn.

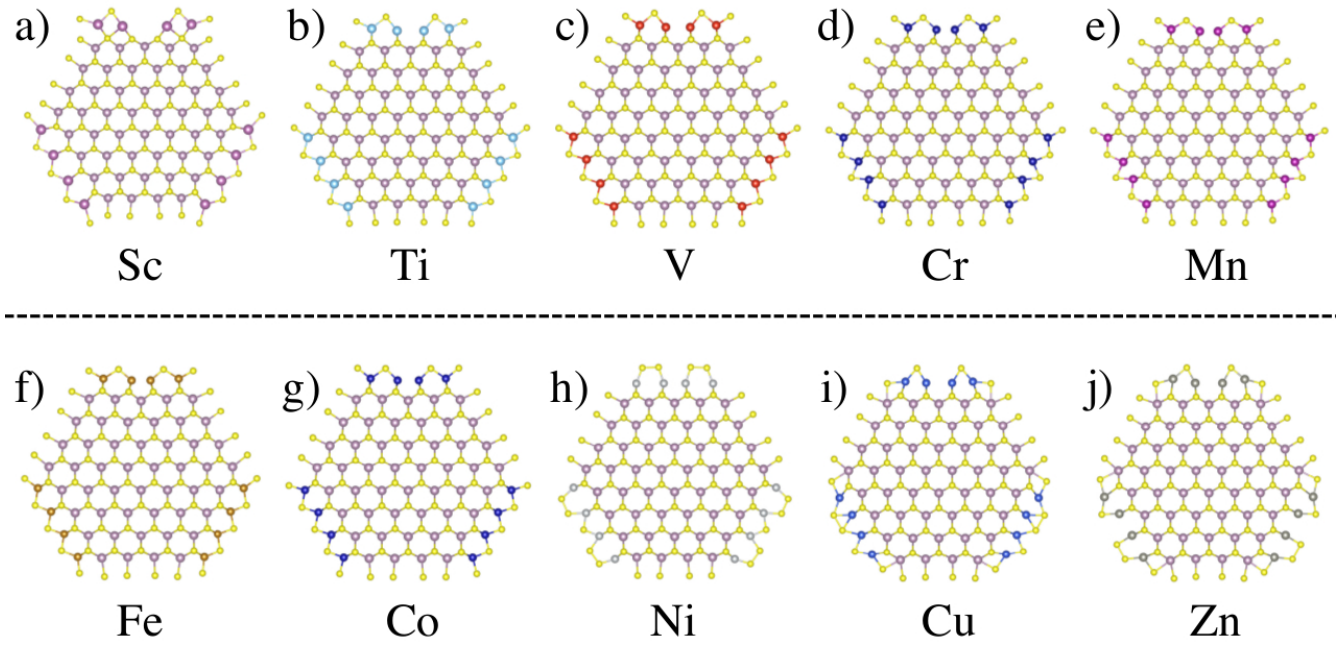


**Fig. S3** Geometrical structures of relaxed TM-promoted $MoS_2$ nanosheets with sulfur vacancy at the center of the edge ($V_S$@Cen), with the 3*d* TM promoters; a) Sc, b) Ti, c) V, d) Cr, e) Mn, f) Fe, g) Co, h) Ni, i) Cu, and j) Zn

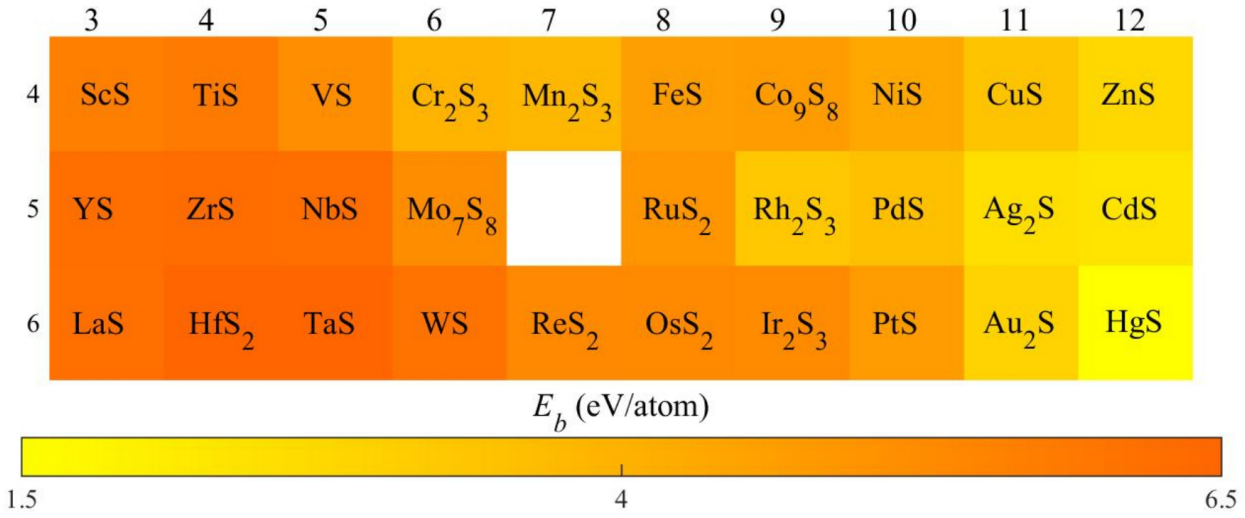


**Fig. S4** Binding energy for the TM-sulfides plotted in rows and columns of the periodic table. Orange means high binding energy, while yellow is for low binding energy.

**Table S1.** Calculated zero-point energy at the adsorbed and isolated state and the entropy of $H_2$, $H_2S$, DBT, and BP at standard conditions (T=298K).

| | $E_{ZPE}$ (eV) | | S° (J/mol K) |
|---|---|---|---|
| | adsorbed | isolated | |
| $H_2$ | 0.51 ($MoS_2$)<br>0.62 (BP) | 0.33 | 130.6[1] |
| $H_2S$ | 0.56 | 0.43 | 205.7[1] |
| DBT | 4.38 | 4.29 | 204.2[2] |
| BP | 4.32 | 4.82 | 209.4[3] |

References


1) D. D. Wagman, W. H. Evans, V. B. Parker, R. H. Schumm, I. Halow, S. M. Bailey, K. L. Churney and R. L. Nuttall, *J. Phys. Chem. Ref. Data*, 1989, **18**, 1807 – 1812.

2) R. D. Chirico, S. E. Knipmeyer, A. Nguyen and W. V. Steele, J. *Chem. Thermodyn.*, 1991, **23**, 431–450.

3) R. D. Chirico, S. E. Knipmeyer, A. Nguyen and W. V. Steele, *J. Chem. Thermodyn.*, 1989, **21**, 1307–1331.

**Table S2.** Calculated binding energy values of the TM-sulfides corresponding to the 3*d*, 4*d*, and 5*d* TM elements.

| | ***3d*** | | ***4d*** | | ***5d*** | |
|---|---|---|---|---|---|---|
| group | TM-sulfides | $E_b$ (eV/atom) | TM-sulfides | $E_b$ (eV/atom) | TM-sulfides | $E_b$ (eV/atom) |
| **3** | ScS | 5.63 | YS | 6.09 | LaS | 6.06 |
| **4** | TiS | 5.74 | ZrS | 6.14 | $HfS_2$ | 6.36 |
| **5** | VS | 5.20 | NbS | 6.09 | TaS | 6.36 |
| **6** | $Cr_2S_3$ | 4.06 | $Mo_7S_8$ | 5.22 | WS | 5.96 |
| **7** | $Mn_2S_3$ | 3.94 | | | $ReS_2$ | 5.32 |
| **8** | FeS | 4.70 | $RuS_2$ | 4.95 | $OsS_2$ | 5.31 |
| **9** | $Co_9S_8$ | 4.75 | $Rh_2S_3$ | 3.48 | $Ir_2S_3$ | 5.25 |
| **10** | NiS | 4.41 | PdS | 3.71 | PtS | 4.78 |
| **11** | CuS | 3.58 | $Ag_2S$ | 2.80 | $Au_2S$ | 3.15 |
| **12** | ZnS | 2.99 | CdS | 2.64 | HgS | 1.85 |